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NONEQUILIBRIUM GASDYNAMICS

by William S. Watt

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FOREWORD

The research reported herein was performed for the National Aeronautics and Space Administration, Fluid Physics Branch, Research Division, Office of Advanced Research and Technology under Contract NASr-109. This contract began in April 1962 and the work performed in the period April 1962 to September 1962 was documented in a Final Report dated September 30, 1962.

The program was renewed in April 1963 and by a series of additions and amendments has been continuous from then until the present (April 1969). The present report provides a complete documentation of the work performed under this contract during the period April 1963 - April 1969. During this period eight CAL reports and nine published articles have been prepared, which represent the contributions of many members of the Aerodynamic Research Department to this contract. The publications and the authors are listed in the Appendix.

INTRODUCTION

The research performed under Contract NASr-109 has been largely concerned with theoretical and experimental studies of nonequilibrium phenomena pertinent to propulsion. In particular, the emphasis was directed toward obtaining a better understanding of the chemistry, fluid mechanics and the coupling of these in hydrogen propulsion systems.

Research has been concentrated in three areas: 1. development of a computer program for the numerical solution of nonequilibrium expansions of reacting gas mixtures and its application to recombination in rocket nozzles; 2. experimental studies of nonequilibrium phenomena in nozzle expansion flows; and 3. experimental studies of dissociation kinetics behind shock waves. While this research program was initially concerned with dissociation and recombination in hydrogen and the effect of catalytic additives on these phenomena, the techniques developed were later extended to investigate other nonequilibrium systems of interest in the propulsion and aerospace fields.

For the purpose of documentation this report is divided into three sections corresponding to the three major research areas. Most of the research performed under this contract has already been documented in CAL reports and the open literature. These areas are described only briefly in this report and the titles and abstracts of the relevant publications are given in the Appendix. Reference to this Appendix is given in the text by superscript numbers preceded by the letter "A". Other sections of the work performed, which are in general less complete and have not been published to date are reported herein.

I. THEORETICAL STUDIES OF HYDROGEN-ATOM
RECOMBINATION IN ROCKET NOZZLES

These studies were concerned with determining the effect of catalytic additives in enhancing atomic recombination in a rocket nozzle environment. The impetus for this work was provided by the loss of specific impulse in chemical propulsion systems caused by thermochemical nonequilibrium.

Initial calculations had suggested that additives such as low molecular weight hydrocarbons[1] which catalyze recombination would help maintain equilibrium by allowing two-body recombination reactions to occur. These bimolecular reactions are much faster than the normal three-body recombination path. Further calculations were performed for hydrogen nozzle flows containing oxygen and an oxygen-nitrogen mixture which demonstrated that gas phase catalysis again increased the specific impulse but that these gains were at least partly offset by the accompanying increase in the molecular weight of the propulsive fluid. These calculations are described in detail in CAL Report AD-1689-A-5.[A1]

Although the addition of catalysts was not found to significantly increase the specific impulse, it was later shown that for the same specific impulse, the catalyzed hydrogen propellant offered a possible saving in tankage volume, and hence structural weight. This feature of the research was published as a technical note in the AIAA Journal.[A2]

An outgrowth of this work and other programs related to nonequilibrium flow properties was the development of a computer program to solve quasi-one-dimensional, inviscid expansions of reacting gas mixtures. This program is designed to handle up to 20 chemical species and 64 reactions and, in addition, allows for vibrational and electronic excitation. The details of this computer code and the many options which are available are given in CAL Report AD-1689-A-6.[A3]

II. EXPERIMENTAL STUDIES OF NONEQUILIBRIUM NOZZLE FLOWS

To calculate the flow occurring in a rocket nozzle or other hypersonic environment, it is necessary to couple the pertinent reaction rate expressions with the gasdynamic equations. The success of these calculations is critically dependent on the accuracy of the rate expressions used for equilibration of vibration, dissociation, ionization, etc. While many of these reaction mechanisms had been studied behind shock waves, few measurements had been made directly in an expanding flow.

Under this contract several experimental studies were made of the nonequilibrium conditions occurring in a nozzle-flow environment. In the first such study the measurement of static pressure distributions along the nozzle wall was used to determine the departure from equilibrium due to freezing of atomic concentrations in gas flows of interest.[A4] For this purpose a hydrogen-argon test gas mixture was processed in a shock tube by incident and reflected shock waves and the high-temperature high-pressure gas behind the reflected shock wave served as a reservoir for a steady-flow expansion in a supersonic nozzle attached to the end of the shock tube.

The result of these experiments was that freezing of the hydrogen atom concentration was observed to have a measurable effect on the pressure distribution. An estimate of the recombination rate constant for hydrogen atoms was obtained from these pressure measurements. These experiments, the results and the conclusions, are described in detail in CAL Report No. AD-1689-A-4[A4] and as a technical note in the AIAA Journal.[A5]

Although these experimental studies were successful they pointed out the need for a diagnostic technique which was more sensitive to flow chemistry.

For this purpose, under other sponsorship, the technique of line-reversal spectrophotometry was developed for vibrational temperature measurements in supersonic nozzle flows.[2]

This technique was then used to monitor flows containing air species which are important in propulsion. Thus, the excitation temperature of sodium which was added to argon and 1% N_2 in argon was examined in nozzle expansion flows.[A6] For pure argon the measured sodium temperatures were considerably in excess of the local translational temperature. This high temperature was interpreted in terms of the excitation of sodium by free electrons which were present in the flow and whose energy was frozen at values corresponding to the throat conditions. For 1% N_2 in argon the measured sodium temperatures were shown to be lower than in pure argon and to correspond to the frozen N_2 vibrational temperatures expected on the basis of previous results.[2] The temperature of the electrons, which were still present, was interpreted to be coupled to the vibrational temperature of the N_2 molecule.

These measurements of free-electron and coupled N_2 vibrational temperatures are described in detail in the Journal of Chemical Physics.[A6] This study led to further investigation of the energy coupling between electrons and molecular vibration, and thermally averaged probabilities for electron de-excitation by the first vibrational level of N_2 were calculated.[A7] This work was also reported in the Journal of Chemical Physics.[A7]

At this time there were several reports in the literature[2-8] that the vibrational relaxation of N_2 proceeded faster in an expansion flow than would be predicted by the Landau-Teller relaxation equation using the rates obtained behind shock waves. A possible explanation was that impurities and/or

electrons which might be present in the gas could enhance the relaxation process and hence might also be important as catalysts for recombination. For this reason a brief study was made of the effect of impurities such as O_2, CO_2, H_2O and C_2H_2 on the vibrational relaxation of N_2 in nozzle expansion flows. This study established that when concentrations of these impurities $\geqslant 10^3$ ppm were added to the test gas, lower N_2 vibrational temperatures were measured. These concentrations were considerably greater than the estimated impurity content of the test gas used but it should be emphasized that the possible effect of impurities in concentrations less than 100 ppm was not established. A note describing the results of this work was published in the Journal of Chemical Physics.[A8]

The lack of a satisfactory explanation for the faster observed relaxation rates of N_2 in the nozzle flow environment prompted a more direct measurement of the vibrational temperatures in expanding flows. A further question of interest was whether N_2 was peculiar in exhibiting this difference in relaxation rates in the two environments.

These queries lead to the extension of the sodium line-reversal technique to use the fundamental, infrared vibration-rotation band (without the need for thermometric additives) of infrared-active molecules. This technique, called band-reversal spectroscopy, was used to measure the vibrational relaxation of CO in both shock-wave and nozzle-flow environments where the test gas was either pure CO or 5% CO in argon. Sodium line-reversal measurements were also made in each environment and these results agreed well with the infrared band-reversal measurements; behind shock waves the results obtained by both techniques compared well with previous measurements of CO relaxation by other investigators. The results of the nozzle flow studies indicate that for CO as well as N_2 the

vibrational relaxation rates are considerably faster than in shock wave flows. This research is reported in detail in a CAL report[A9] and in the **Journal of Chemical Physics.**[A10]

Following the CO relaxation studies band-reversal spectroscopy was used to measure the vibrational relaxation of CO_2 in both shock-wave and nozzle-expansion flows by monitoring the vibrational temperature of the ν_3 asymmetric stretching mode.

The vibrational relaxation time for CO_2, and for CO_2 diluted in other gases, has been measured at room temperature by several techniques.[9] However, at elevated temperatures there are few measurements, and above 1500°K there is only one measurement, which was in pure CO_2.[10] This measurement showed that the vibrational relaxation time was less than 1 μsecond at 1 atmosphere and decreased by approximately a factor of 2 between 1500°K and 3000°K. In the present study, apparatus limitations prevented the measurement of these short relaxation times. However, dilution of CO_2 with 90% argon slowed the relaxation process sufficiently to allow relaxation measurements to be made behind incident shock waves. These data were obtained in the temperature range 1500°K to 2500°K and are shown in Figure 1. Also shown are the fits to the experimental data for pure CO_2 suggested by Camac[10] and by Carnevale, Carey and Larson (CCL).[11] To obtain the vibrational relaxation time for CO_2 infinitely dilute in argon, τ_{CO_2-Ar}, from the present measurements a value for pure CO_2 relaxation time, $\tau_{CO_2-CO_2}$, was required. Assuming Camac's value for $\tau_{CO_2-CO_2}$ it was found that $\tau_{CO_2-Ar} / \tau_{CO_2-CO_2} \approx 5.5$ while taking the CCL data it was found that $\tau_{CO_2-Ar} / \tau_{CO_2-CO_2} \approx 4.5$. Measurements[9] suggest that this ratio is about seven at room temperature.
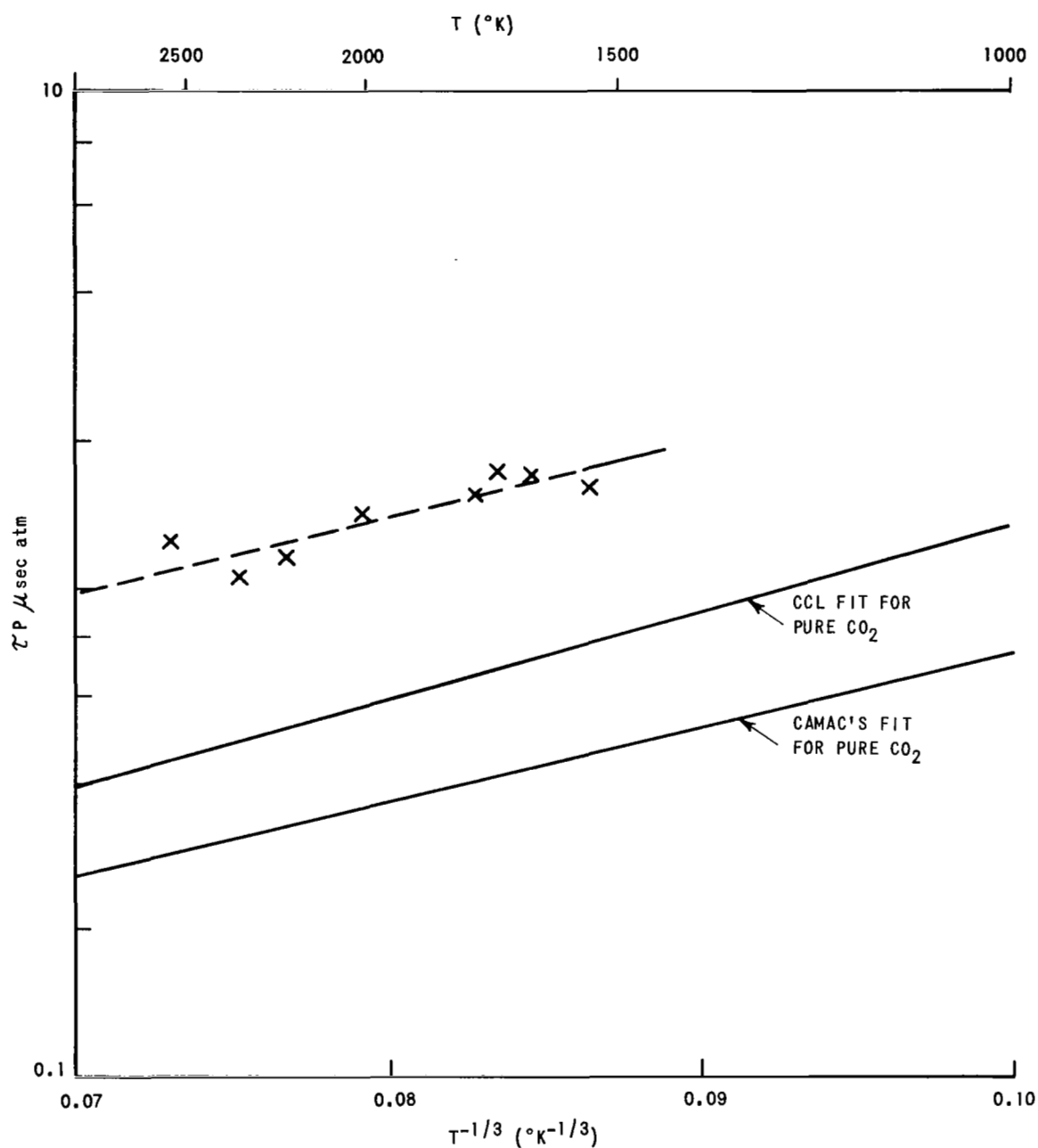
Figure 1 VIBRATIONAL RELAXATION TIMES FOR 10% CO_2 IN ARGON
BEHIND INCIDENT SHOCK WAVES

In the supersonic nozzle expansion of the gas behind the reflected shock, the rate of cooling is determined by the molecular weight and the ratio of the specific heats, γ, of the expanding gas. For pure CO_2 (γ = 1.32) the gas cools rather slowly. This effect, coupled with the rapid vibrational relaxation of CO_2, allows the vibrational temperature of CO_2 to remain in equilibrium with the translational temperature except at very low reservoir pressures (< 1 atm). Reservoir pressures in this range cannot readily be produced in the existing facilities and hence the relaxation of pure CO_2 in expanding flows was not studied.

Dilution of CO_2 with argon does not greatly affect the molecular weight of the gas, but increases γ substantially, thus providing much faster cooling rates at high dilutions. As a result a departure from equilibrium and subsequent vibrational freezing can be expected for attainable reservoir pressures. Measurements have been made in expanding flows at a local-to-throat area ratio (A/A^*) of eight in gas mixtures whose initial composition was 10 % CO_2 in argon. The reservoir temperature and pressures were in the ranges 3000°K - 3900°K and 6 - 20 atmospheres.

With the band-reversal technique, vibrational temperatures which lie within approximately 500°K of the temperature of the background radiation source can be measured. For the radiation source used, this temperature range was approximately 900°K - 1900°K. In the present experiments, nozzle vibrational temperatures T_v in the range 900°K - 1300°K were measured at A/A^* = 8 in gases whose reservoir conditions are given above. At lower reservoir temperatures the vibrational temperature is too low to be measured, and at higher reservoir temperatures the CO_2 is almost completely dissociated in the reservoir. In addition, application of Bray's freezing criterion[12] indicates that chemistry in the nozzle is essentially frozen at the reservoir conditions and hence the CO_2 is

not regenerated. This was taken into account in computing the properties of the expanding flow since the temperatures for chemically frozen flow are somewhat lower than equilibrium temperatures and hence lower nozzle vibrational temperatures are predicted.

In Figure 2 the frozen-flow translational temperature distribution along the nozzle axis is shown for 10 % CO_2 in argon ($\tau = 0$). In addition, the vibrational temperatures predicted by the Landau-Teller relaxation model by assuming the shock tube vibrational relaxation time ($\tau = \tau_s$) and one tenth the shock tube relaxation ($\tau = 0.1\tau_s$) are shown. The data are for the reservoir conditions indicated and suggest that the CO_2 relaxes in an expanding flow at a rate similar to the measured shock tube relaxation rate. This is in contrast to the results previously reported for CO[A9, A10] and N_2[2-8] which were found to relax more rapidly in expansion flows than in shock wave flows.

However, it should be noted that the kinetic processes do not simply involve a mixture of CO_2 in argon. Carbon monoxide and oxygen molecules as well as oxygen atoms are present in significant amounts (50 % of the CO_2 is dissociated at 3300°K and 6 atmospheres) and can allow relaxation to occur by several possible mechanisms whose net effect is unknown.

The data for 10 % CO_2 in argon are shown in Figure 3 as a function of reservoir temperature. The experimental data have been normalized to a reference reservoir pressure of 10 atmospheres. The curves labeled $\tau = \tau_s$ and $\tau = 0.3\tau_s$ represent the vibrational temperatures expected on the basis of the Landau-Teller relaxation model if the measured shock-tube relaxation time (τ_s) and three-tenths this time apply to relaxation in expansion-flow environments. The data are seen to fall between these curves and are interpreted as suggesting that CO_2 in CO_2 argon mixtures relaxes at approximately the same rate in shock-wave and in expansion-flow environments.
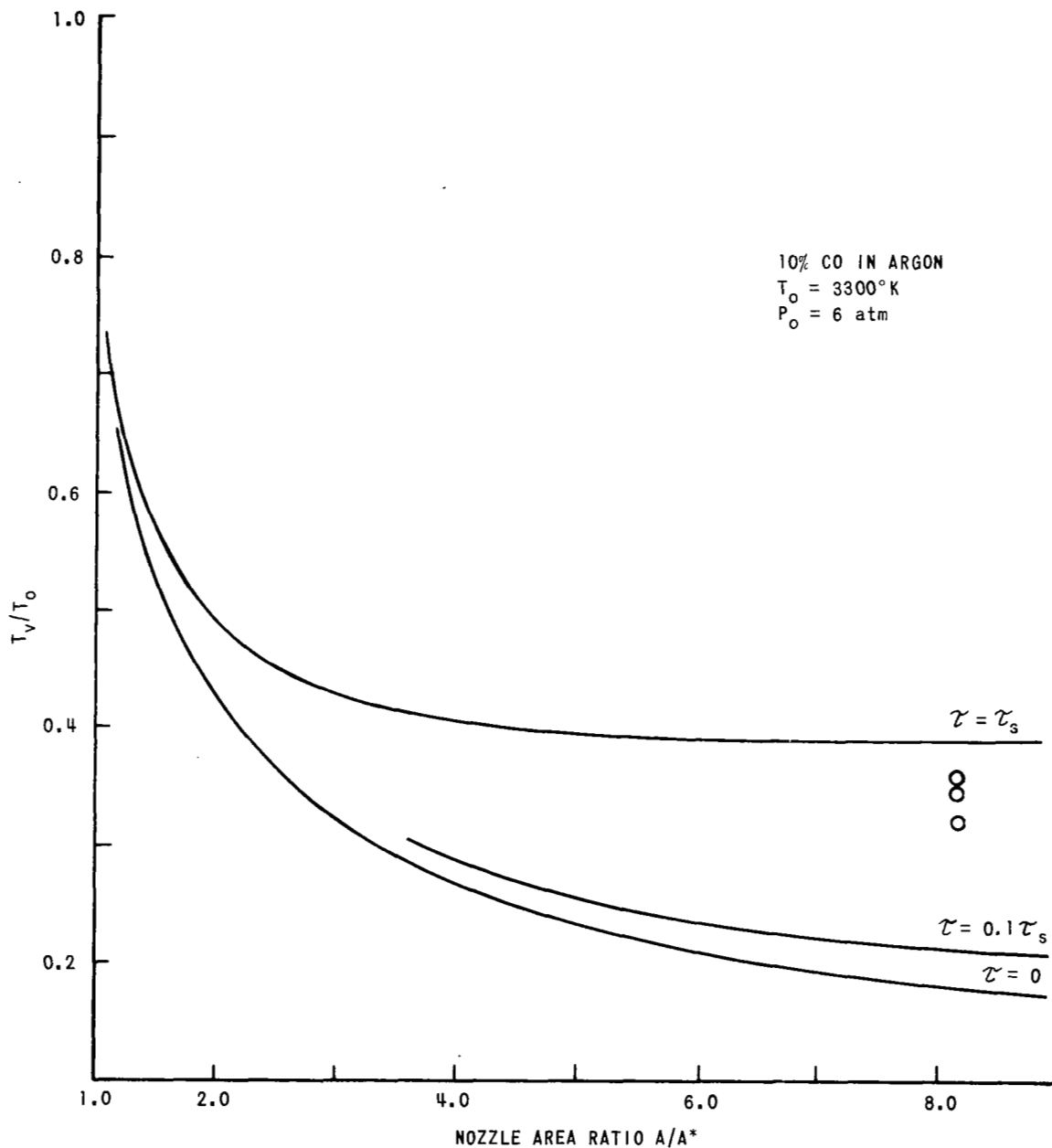
Figure 2   VIBRATIONAL TEMPERATURE/RESERVOIR TEMPERATURE (T_V/T_O) AS A FUNCTION
OF NOZZLE AREA RATIO.   O - EXPERIMENTAL DATA; CURVES SHOW THE VALUES
OF T_V/T_O PREDICTED BY THE LANDAU-TELLER RELAXATION THEORY FOR $\tau = \tau_s$,
$\tau = 0.1\tau_s$ AND $\tau = 0$

Figure 3 VIBRATIONAL TEMPERATURE/RESERVOIR TEMPERATURE (T_v/T_o) AS A FUNCTION OF RESERVOIR TEMPERATURE. X – EXPERIMENTAL DATA; CURVES SHOW THE VALUES OF T_v/T_o PREDICTED BY THE LANDAU–TELLER RELAXATION THEORY FOR $\tau = \tau_s$, $\tau = 0.3\ \tau_s$ AND $\tau = 0$.
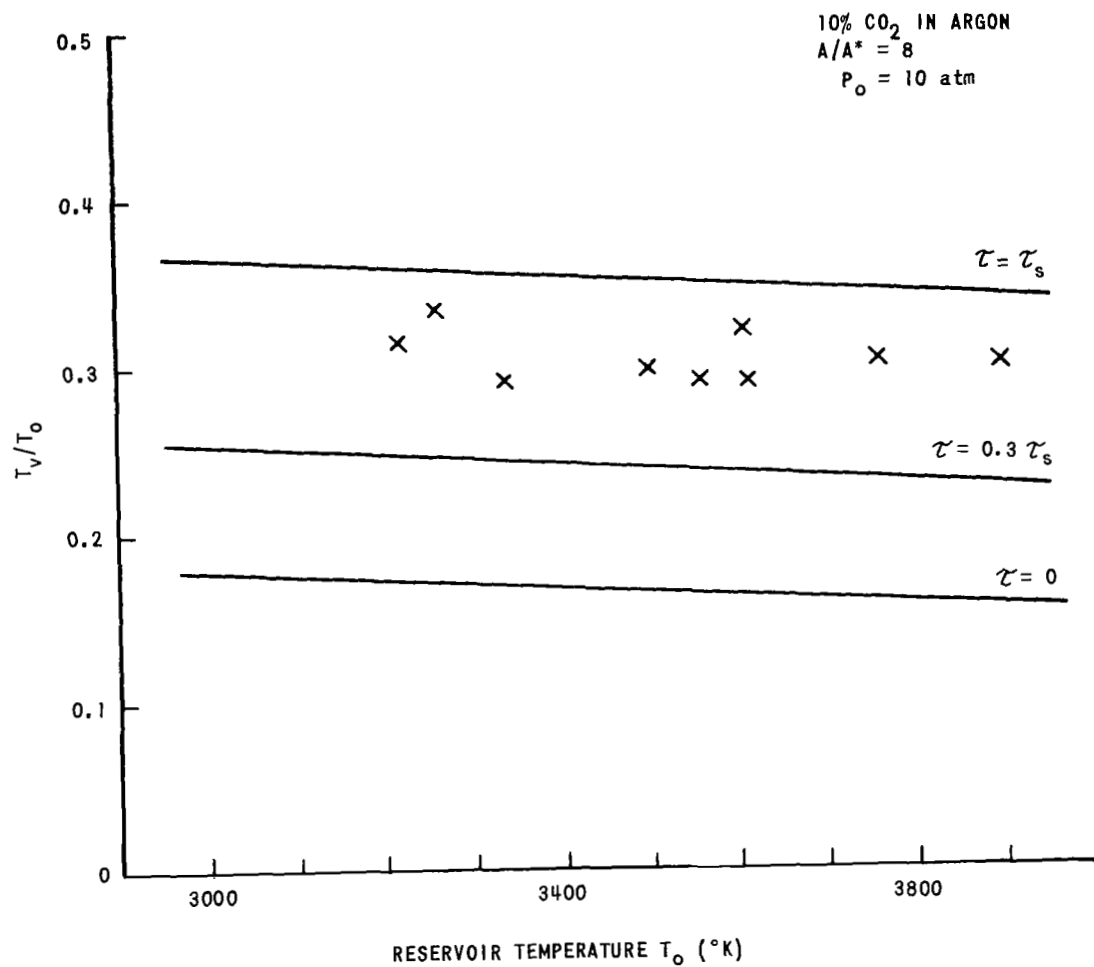
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III. DISSOCIATION KINETICS BEHIND SHOCK WAVES

Throughout this contract, work was also directed to resolving the dissociation kinetics of simple molecules of interest in propulsion. These studies have centered around the technique of atomic resonance absorption spectrophotometry which was adapted under this contract to be suitable for making transient measurements of atomic concentrations in the nonequilibrium region behind shock waves.

The initial emphasis was toward obtaining more accurate rate-constant measurements for hydrogen dissociation and to determining the effect of catalytic additives on the dissociation process. To this end much of the early work was directed toward the development of a continuously operating radiation source which would generate the desired atomic radiation with sufficient intensity for shock wave absorption studies.

This initial development of a vacuum ultraviolet light source and the feasibility of the technique for monitoring hydrogen atoms by their absorption at the Lyman α wavelength (1215.7 Å) is described in considerable detail in CAL Report No. AD-1689-A-3.[A11] A note describing these initial results was published in the Journal of Chemical Physics.[A12]

One of the results of the investigation was that the sensitivity of this technique required the construction of a shock tube facility in which the purity of the test-gas mixture could be maintained within a few parts per million. Such a facility was built with CAL funding and was used for the subsequent dissociation studies under this contract. With this facility the dissociation rate constants for hydrogen with argon and hydrogen as collision partners were determined. In addition, the catalytic effect of small amounts of oxygen was

determined. These latter measurements led to a determination of the rate for the reaction $H + O_2 = OH + O$. This work was reported in CAL Report No. AD-1689-A-7.[A13]

This work was extended to include a direct experimental determination of the hydrogen atom absorption coefficient. These data were used to obtain more accurate rate constants for hydrogen dissociation and the effect of added oxygen. These results are published in the Journal of Chemical Physics.[A14]

Following the completion of the hydrogen atom studies this technique was used to monitor oxygen atom formation rates behind shock waves in oxygen, nitric oxide and carbon dioxide. The oxygen atoms were monitored by their absorption at the oxygen resonance triplet near 1300 Å which was generated by RF excitation of He/O_2 gas mixtures in the radiation source. The absorption coefficient at this wavelength was determined experimentally.

For oxygen-argon mixtures the observed rate of atom formation has allowed a determination of the dissociation rate constant for oxygen in argon. In addition it was found that this technique was ideally suited to making measurements of vibration- dissociation coupling. The induction time for establishing steady atom formation rates was measured and compared with previously measured[13] and predicted[14] induction times for the oxygen-argon system. The present measurements indicate induction times considerably longer than predicted and may provide a basis for improvements to be made in the theoretical models used to describe vibration-dissociation coupling.[14]

These measurements of dissociation and vibration-dissociation coupling in oxygen are documented in CAL Report No. AD-1689-A-9[A15] and in a paper which has been accepted for publication in the Journal of Chemical Physics.[A16]

Following the completion of the study of the oxygen-argon system, attention was focused on other systems which produced oxygen atoms upon dissociation, i.e. CO_2 and NO. In these systems the oxygen atoms take part in additional reactions which complicate the kinetic mechanism for atom production. The data obtained for these two systems will now be presented and discussed.

CO_2 - Argon

The simple dissociation of CO_2 proceeds via

$$CO_2 + M \longrightarrow CO + O + M \qquad\qquad 1.$$
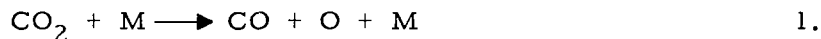
but in the presence of CO_2, atomic oxygen reacts further by

$$CO_2 + O \longrightarrow CO + O_2 \qquad\qquad 2.$$

and the oxygen produced in reaction 2 dissociates by

$$O_2 + M \longrightarrow O + O + M \qquad\qquad 3.$$

The rate of atom formation is thus a function of three concurrent reactions. In the test time of the present experiments the amount of O_2 formed by reaction 2 is small compared with the CO_2 present. Hence, since CO_2 and O_2 have similar dissociation energies, reaction 3 can be ignored in the data analysis. For the oxygen atom concentration required for measurable absorption at 1300 Å, reaction 2 becomes less important as the CO_2 concentration is reduced. Approximate calculations indicated that for the conditions of the present experiments reaction 2 should become unimportant when the CO_2 concentration is reduced below 1% CO_2 in argon.

In Figure 1 the oxygen atom formation rates from mixtures of 1 % and 0. 1 % CO_2 in argon are shown. The data are presented as $k_d = (d[o]/dt)/[CO_2][M]$ where k_d becomes the dissociation rate constant for CO_2 when reaction 2 is unimportant.

In the temperature range 3500°K - 6000°K the data presented clearly indicate a higher value of k_d (and a higher activation energy) for lower CO_2 concentration. The k_d for 0. 1 % CO_2 in argon can be compared with the results of Davies[15, 16] who obtained three different sets of rate constants for reaction 1 as he monitored different types of radiation from CO and CO_2. For example, at 5550°K the k_d in the present work is approximately twice that found by Davies in uv radiation studies of the CO flame bands[15] but about one half of the value he obtained from infrared measurements of CO_2 emission at 2.7 μ or 4.3 μ.[16] The apparent activation energy of the present results $\sim$ 81, 000 cal. $mole^{-1}$ is to be compared with the values of $\sim$ 86, 000 cal. $mole^{-1}$ from uv and $\sim$ 73, 000 cal. $mole^{-1}$ from ir found by Davies.

The present results are insufficient to determine whether the data for 0. 1% CO_2 in argon are indicative only of the dissociation process. However, since the ratio of oxygen atoms to argon atoms is $\leq 10^{-4}$ these data indicate that $k_2/k_1 \geq 10^4$ in the temperature range investigated.

Dissociation of CO_2 to give ground state oxygen atoms, $O(^3P)$, is spin forbidden and would thus be expected to be a slow process. The spin allowed process

$$CO_2(^1\Sigma) \longrightarrow CO(^1\Sigma) + O(^1D) \qquad\qquad 4.$$
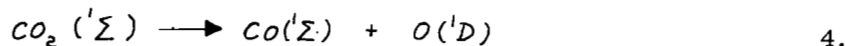
is more probable but requires considerably more energy than dissociation to $O(^3P)$. In addition, since the concentration of $O(^3P)$ is the measured quantity,
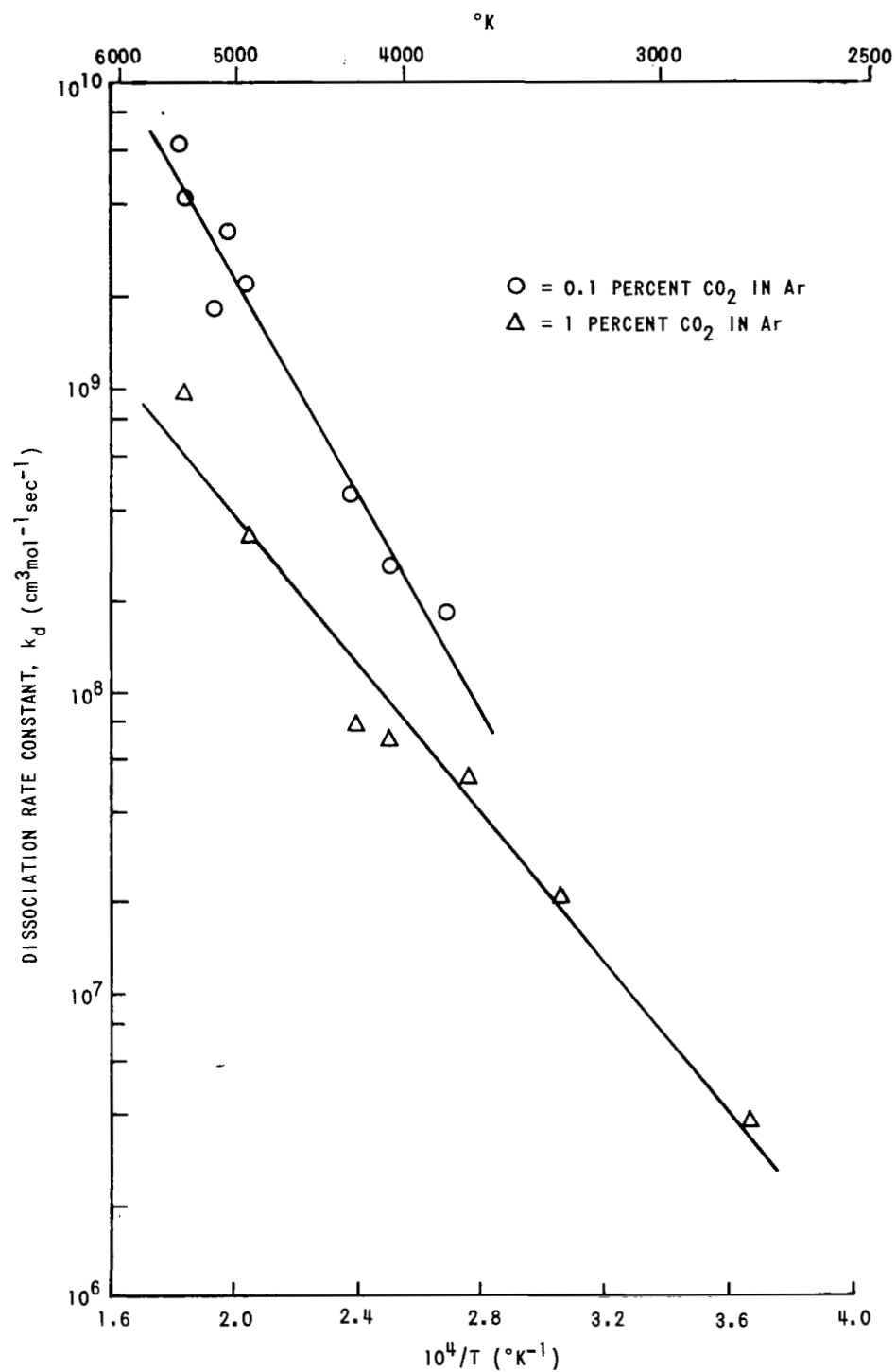
Figure 4 ARRHENIUS PLOT OF THE EXPERIMENTAL DATA FOR THE DISSCCIATION RATE
CONSTANT OF CO_2 IN 1 PERCENT AND 0.1 PERCENT CO_2 - Ar MIXTURES

the deactivation of $O\,(^1D\,)$ to $O\,(^3P\,)$ would have to be considerably faster than the dissociation process for the present technique to measure the dissociation rate. In collisions with argon the known deactivation rate for $O\,(^1D\,)$ is too slow[17] to allow this interpretation. Although CO_2 is more efficient for deactivating $O\,(^1D\,)$ there is considerable controversy about the magnitude of the rate,[17] thus preventing an assessment of the effect of the CO_2 present.

The present results for 0.1% CO_2 in argon, which suggest a low activation energy and an apparent rate constant comparable to that of Davies, seem to suggest that dissociation occurs to ground state products and that spin conservation rules are unimportant in CO_2 dissociation.

NO - Argon

Determinations of the rate of oxygen atom formation behind shock waves in mixtures of 10%, 1% and 0.1% NO in argon have been made in the temperature range 3000°K to 7200°K. Under these conditions, the dissociation of NO and the subsequent reactions of the products should proceed by the following mechanism:

$$NO + Ar \longrightarrow N + O + Ar \qquad\qquad 5.$$
$$NO + N \longrightarrow N_2 + O \qquad\qquad 6.$$
$$NO + O \longrightarrow O_2 + N \qquad\qquad 7.$$

The rate of oxygen atom formation is thus a function of the rates of these reactions. At high concentrations of NO the reaction

$$NO + NO \longrightarrow N_2O + O \qquad\qquad 8.$$

may also contribute to oxygen atom formation.

The rate constants for atom formation defined as $k_d = (d[O]/dt)/[NO][Ar]$ the k_d obtained for 10%, 1% and 0.1% NO in argon, are shown in Fig. 5. In the temperature range 5000°K - 7000°K there is a definite increase in k_d as the
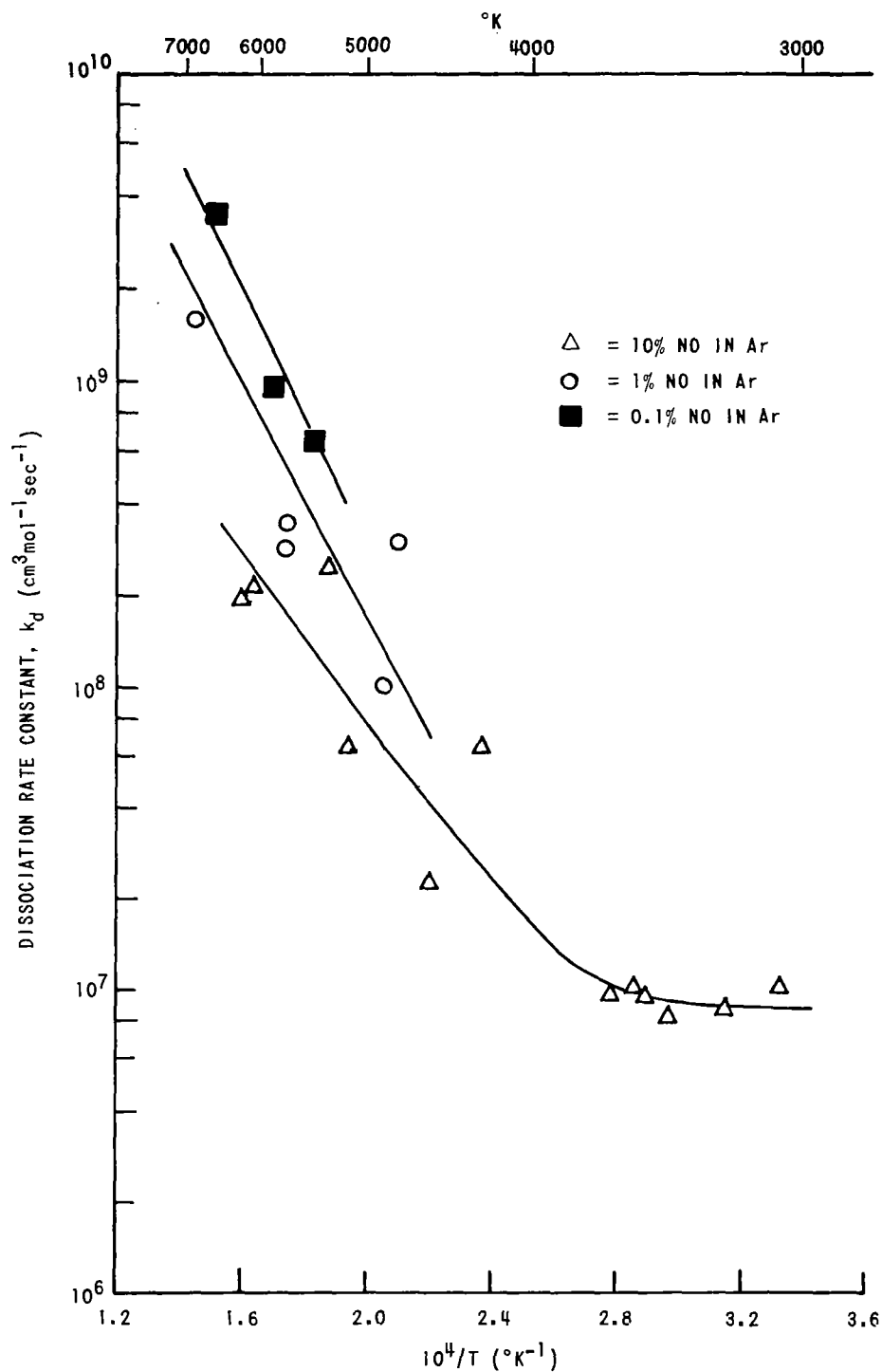
Figure 5   ARRHENIUS PLOT OF EXPERIMENTAL DATA FOR THE DISSOCIATION RATE CONSTANT
OF NO IN 10 PERCENT, 1 PERCENT AND 0.1 PERCENT NO - Ar MIXTURES

NO concentration is decreased, but the considerable scatter among the data especially at the higher NO concentrations prevents meaningful interpretation in terms of the reactions discussed above. The k_d obtained for 0.1% NO in argon agree closely with the recent data of Camac and Feinberg[18] for the dissociation of NO, which suggests that, at this concentration of NO, the true NO dissociation rate is directly given by the rate of appearance of oxygen atoms. However, the present data are too few to allow a reliable estimate of the rate constant expression for this process.

While the work on the dissociation of CO_2 and NO was in progress the emphasis of the program was redirected toward reactions of interest to chemical laser systems. Thus, these phases of the contract were terminated before they were complete and the results described above are not published elsewhere.

With the current emphasis on chemical lasers it was of importance that atomic absorption spectroscopy was ideally suited to studying reactions such as

$$Cl + HBr \longrightarrow HCl + Br \qquad\qquad 9.$$
and
$$Cl + HI \longrightarrow HCl + I \qquad\qquad 10.$$
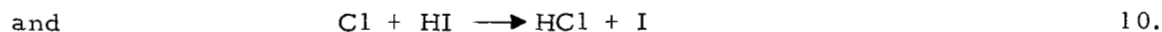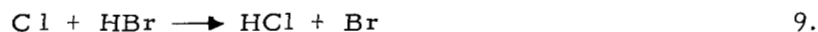
Both of these reactions are exothermic and produce vibrationally excited HCl.[19] The second reaction is the basis of the most powerful HCl laser known to date.[20] In both of these cases, as with HF lasers, the atom concentration is an essential aspect of the inversion mechanism.

In order to study these reactions by the resonance absorption of the atoms it was necessary to produce a source which emitted the required radiation, to determine experimentally the atomic absorption coefficient, and to test the technique on a simple reaction mechanism. A convenient system was the dissociation of HBr diluted in argon.

It was found that bromine-atom transitions between 1480 Å and 1640 Å were emitted when a flow of a few percent HBr in helium was excited in the vacuum ultraviolet light source previously described.[All] The radiation at 1580 Å was most intense and thus used for the kinetic measurements. This radiation consists of three transitions $4p^5\ ^2P^o_{1/2} \rightarrow 5s'\ ^2P^o_{3/2}$, $4p^5\ ^2P^o_{3/4} \rightarrow 5s\ ^4P_{5/2}$ and $4p^5\ ^2P^o_{1/2} \rightarrow 5s'\ ^4P_{1/2}$ whose relative intensities are unknown. For the measurements reported here, the bandpass of the monochromator (16 Å) included all three transitions and thus atoms in both the $^2P^o_{3/2}$ and $^2P^o_{1/2}$ states absorb radiation in this wavelength region.

Emission corresponding to transitions to the $^2P^o_{1/2}$ level are observed in the nonequilibrium environment of the light source. However, for the shock wave environment this level is unlikely to exceed its equilibrium population. Since this level lies 3685 cm^{-1} above the ground state, less than 12% of the Br atoms are in the $^2P^o_{1/2}$ level for the temperatures of interest here.

To determine the absorption coefficient of Br atoms at 1580 Å, the absorption by known Br atom concentrations, produced in the equilibrium region behind incident shock waves, was measured. The atom concentrations were prepared by shock heating gas mixtures of ∼200 ppm HBr or CH_3Br in argon to temperatures in the range 2150 °K to 4000°K. Under these conditions complete dissociation occurs during the available test-time and a steady bromine absorption level is obtained. The absorption coefficient is determined by using Beer's Law and the known bromine atom concentration.

Figure 6 shows the measured absorption coefficients K_ν as a function of gas temperature. The values obtained are essentially temperature independent up to 3000°K and increase with temperature above this point. The transitions from the $^2P^o_{1/2}$ level have somewhat larger absorption coefficients than that from the $^2P^o_{3/2}$ level. However, the increase in population in the $^2P^o_{1/2}$ level with temperature is not sufficient to explain the observed temperature dependence.
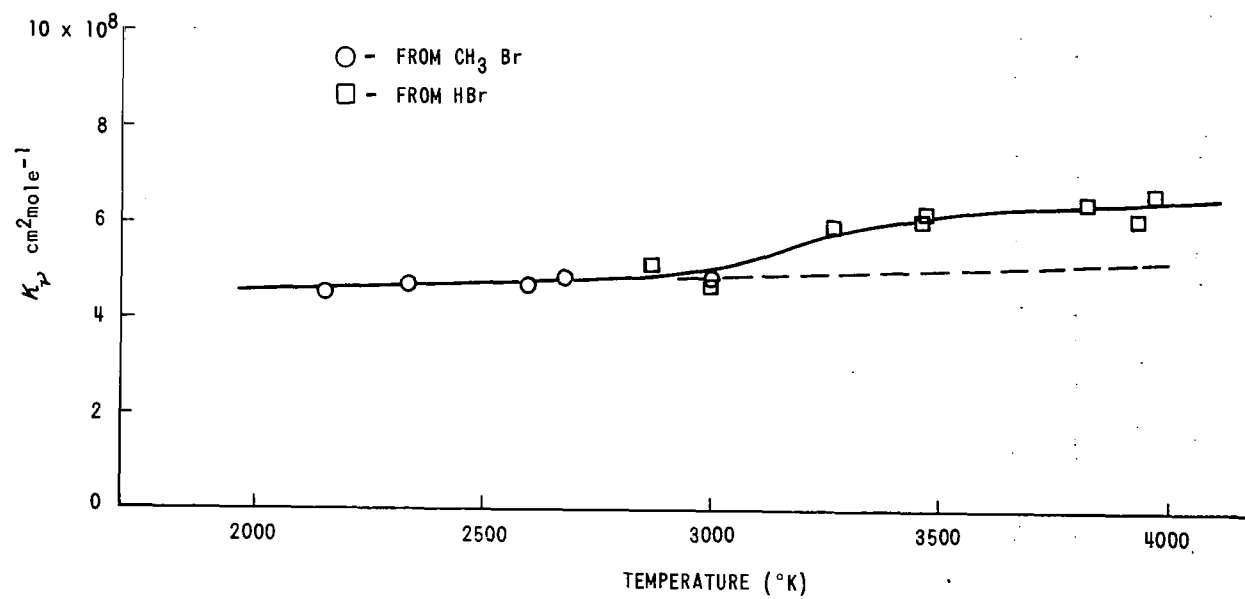
Figure 6   MEASURED BROMINE ATOM ABSORPTION COEFFICIENT AT 1580 Å

From the given relative intensities of the transitions the overall absorption coefficient should rise by approximately 10% in the interval 2000°K to 4000°K, as is indicated by the broken line in Figure 6.

While considering this temperature dependence of the absorption coefficient it is noted that in general the data below 3000°K were obtained with CH_3Br-Ar mixtures while the higher-temperature data were obtained with HBr-Ar mixtures. For the test-time available, HBr was completely dissociated at temperatures 3000°K. At lower temperatures CH_3Br was used to ensure that complete dissociation was attained within the test-time. There is no apparent reason for the two gases to lead to different absorption coefficients for the bromine atom.

The dissociation of HBr in argon proceeds by

$$HBr + Ar \longrightarrow H + Br + Ar \qquad\qquad 11.$$

which may be followed by the reactions

$$H + HBr \longrightarrow H_2 + Br \qquad\qquad 12.$$

$$Br + HBr \longrightarrow Br_2 + H \qquad\qquad 13.$$

$$Br_2 + Ar \longrightarrow 2Br + Ar \qquad\qquad 14.$$

$$H_2 + Ar \longrightarrow 2H + Ar \qquad\qquad 15.$$

As will be shown later, the data indicate that reactions 12 and 15 are occurring. The small bromine atom concentration and the endothermicity of reaction 13 makes this reaction unimportant during the test time of the present experiments.

Thus

$$d(Br)/dt = k_{11}(HBr)(Ar) + k_{12}(H)(HBr) \qquad\qquad 16.$$

and before an appreciable H_2 population builds up

$$d(H)/dt = k_{11}(HBr)(Ar) - k_{12}(H)(HBr) \qquad 17.$$

Measurements of the bromine atom formation rate have been made throughout the temperature range 1750°K to 4000°K for mixtures of 1% and 0.15% HBr in argon at shocked gas pressures in the range 0.3 - 1.0 atmospheres. Hydrogen atom formation rates have been measured at a few temperatures in this range and have been found to be about 10% of the bromine atom formation rate.

Thus to a first approximation

$$dBr/dt = 2 k_{11}(HBr)(Ar) \qquad 18.$$

The values of the dissociation rate constant k_{11} obtained from the bromine atom formation rates via equation 18 are given in Figure 7. In the data reduction the absorption coefficients given by the solid line in Figure 6 were used. The line through the data in Figure 7 corresponds to a dissociation rate constant given by

$$k_{11} = 9.5 \times 10^{11} \exp(-50,500/RT) \ cm^3 \ mole^{-1} \ sec^{-1}$$

The activation energy is to be compared with the bond dissociation energy of 86 kcal mole^{-1}.

Also shown in Figure 7 are the dissociation rate constants for HCl in argon[21] and HF in argon.[22] For these hydrogen halides the measured activation energies are ~ 75 kcal mole^{-1} and 108 kcal mole^{-1} which are also lower than their dissociation energies of 102 kcal mole^{-1} and 134 kcal mole^{-1}.

Returning to the hydrogen atom formation rates, it is noted that Equ. 17 predicts that the hydrogen atom concentration should eventually reach a steady state. Although the rate of formation of this atom was observed.
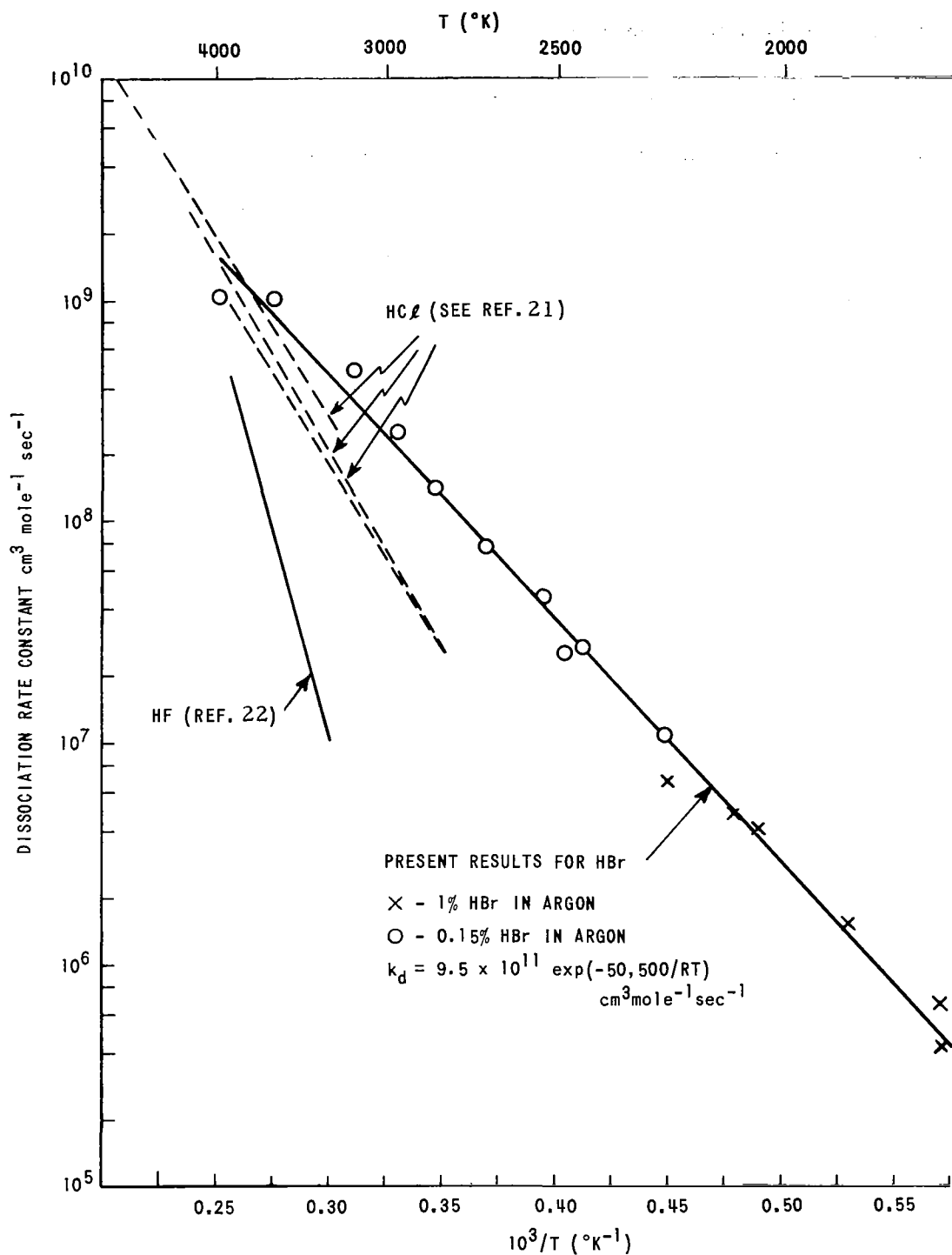
Figure 7   MEASURED RATE CONSTANTS FOR DISSOCIATION OF HYDROGEN HALIDES

The figure shows a plot of DISSOCIATION RATE CONSTANT $cm^3 mole^{-1} sec^{-1}$ (y-axis, from 10^5 to 10^{10}) versus $10^3/T$ ($°K^{-1}$) (x-axis, from 0.25 to 0.55). The top axis shows T (°K) with markings at 4000, 3000, 2500, and 2000.

Labels on the figure:
- HCℓ (SEE REF. 21)
- HF (REF. 22)

PRESENT RESULTS FOR HBr

$\times$ - 1% HBr IN ARGON
$\bigcirc$ - 0.15% HBr IN ARGON
$k_d = 9.5 \times 10^{11}$ exp(-50,500/RT)
          $cm^3 mole^{-1} sec^{-1}$

to decrease from its initial value, a steady state is not observed but a lower constant appearance rate is attained. This phenomenon suggests that the dissociation of hydrogen, produced in reaction 12, is now contributing to hydrogen atom formation by reaction 15. Calculation of the extent of reactions 12 and 15 confirms that this interpretation provides a reasonable explanation for the observed time dependence of the hydrogen atom concentration. Since the rate constants for reactions 11 and 15 are known, direct integration of the hydrogen atom concentration produced in reactions 11, 12 and 15 would allow the rate constant for reaction 12 and its temperature dependence to be evaluated. This has not been attempted as insufficient data are available at this time. However, with the available data it is possible to place k_{12} in the range 10^{12} - 10^{13} cm^3 $mole^{-1}$ sec^{-1} which is to be compared with the value 6×10^{12} cm^3 $mole^{-1}$ sec^{-1} at $500°K$ used by others.[23]

In conclusion, it has been shown that the technique of atomic resonance spectrophotometry is a sensitive method for examining kinetic processes involving atoms. In particular, the high sensitivity to atoms allows reaction schemes to be studied at early times in dilute systems where the atom concentrations are small. In dissociation measurements this feature permits the unambiguous determination of the efficiency of a single collision partner. In more complex kinetic schemes this advantage allows primary and secondary reactions to be investigated individually.

ADDENDUM

During the final stages of the preparation of this report, a publication entitled, "The Dissociation of HBr in Shock Waves" by R. R. Geidt, N. Cohen and T. A. Jacobs[24] was received. These authors measured the rate of dissociation of HBr by its absorption of radiation at 2350 Å and by its infrared emission near 4μ. The rate constant expression reported by these authors for dissociation of HBr in argon is

$$k_{HBr-Ar} = 1.55 \times 10^{12} \exp(-50,000/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

This result is in excellent agreement with the present data and was obtained for the same temperature range.

APPENDIX

In this section a listing is given of the reports and papers prepared under Contract NASr-109. The abstracts of these publications are given.

REPORTS ISSUED

A. 1 Catalysis of Hydrogen Atom Recombination in Rocket Nozzles,

J. A. Lordi and R. E. Mates, CAL Report No. AD-1689-A-5, July 1965.

Abstract

The use of gas-phase catalysis has previously been suggested as a means of enhancing hydrogen-atom recombination and hence the performance of nuclear or electrically powered rocket engines. In an earlier study the use of carbon addition was examined by obtaining numerical solutions for nonequilibrium expansions of carbon-seeded hydrogen. In the present study the use of oxygen and an oxygen-nitrogen mixture as catalysts has been examined. The results of the calculations indicate, as do earlier solutions using carbon addition, that gas-phase catalysis leads to a marginal increase in specific impulse. In both instances hydrogen-atom recombination was significantly enhanced, but the accompanying increase in the molecular weight of the fluid led to slight losses or gains in specific impulse depending on the reaction-rate constants employed for the catalytic mechanisms.

Both the results of the present studies and those of the hydrogen-carbon system are used to establish the minimum requirements which an additive must satisfy to yield a gain in specific impulse. An expression is derived for a "catalytic parameter" which gives an approximation for the gain in performance which can be expected for a given additive. Also, the results of both studies show that a significant saving in tankage weight may be possible despite only marginal gains in specific impulse.

A. 2 Possible Weight Saving from Catalysis of Recombination in Hydrogen

Rockets, J. A. Lordi, R. E. Mates and A. Hertzberg, AIAA J. 6, 172

(1968).

A. 3 Computer Program for the Numerical Solution of Nonequilibrium

Expansions of Reacting Gas Mixtures, J. A. Lordi, R. E. Mates and

J. R. Moselle, CAL Report No. AD-1689-A-6, October 1965.

A. 3 cont'd. Abstract

This report describes a computer program developed at CAL for the numerical solution of quasi-one-dimensional, inviscid expansions of reacting mixtures. The analytical techniques employed and results obtained using the program have been previously reported. The details of the coding and operation of the program are discussed in this report. Program cards which have been written in FORTRAN IV language for use on an IBM 7044 computer are available upon request.

The computer program in its present form is capable of handling a general gas mixture, including up to 20 chemical species and 64 reactions. The species are assumed to undergo vibrational and electronic excitation in addition to coupled chemical reactions. The vibrational and electronic degrees of freedom are assumed to remain in thermodynamic equilibrium while the chemical reactions may be assumed to be either frozen, in equilibrium, or to proceed at finite reaction rates. Additional options in the program are provided for treating ionized nozzle flows, assuming the degree of vibrational excitation to be frozen at the reservoir value, or including the effects of moderate virial imperfections on high-density nozzle flows.

While the basic program computes the properties of an expansion from an equilibrium reservoir state through a nozzle of specified geometry, modifications of the program have been made to permit specifying the streamtube pressure variation rather than an area distribution and to permit a finite-velocity, equilibrium or nonequilibrium initial state. The program cards for these modified versions of the program are also available upon request.

A. 4 Experimental Studies of Chemical Nonequilibrium in Hydrogen Nozzle Flows, A. L. Russo, J. G. Hall and J. A. Lordi, CAL Report No. AD-1689-A-4, June 1964.

Abstract

The effects of finite recombination rates on the flow of highly dissociated hydrogen in an argon bath have been studied in supersonic nozzle expansion flows of shock heated H_2/Ar mixtures. Nozzle-wall static pressure distributions have been obtained for expansions from a reservoir temperature of 6000°K and reservoir pressures of 28, 57 and 112 atm. The measured pressures show a definite departure from the values expected for equilibrium flow, and this is interpreted as due to lag in H-atom recombination during the flow expansion. Recombination rate constants were determined to about a factor of 2.5 by comparing the experimental pressure data with exact numerical calculations. The mean values of these recombination rate constants were found to be in agreement with corresponding rate constants deduced from shock-wave dissociation results.

A. 5   Measurements of Nonequilibrium Static Pressures in Nozzle Flows of
       Dissociated Hydrogen, A. L. Russo, J. G. Hall and J. A. Lordi, AIAA J.
       <u>4</u>, 741 (1966).

A. 6   Spectrum-Line Reversal Measurements of Free-Electron and Coupled
       N_2 Vibrational Temperatures in Expansion Flows, I. R. Hurle and
       A. L. Russo, J. Chem. Phys. <u>43</u>, 4434 (1965).

                              Abstract

        Spectrum-line reversal measurements of the excitation temperature of Na
atoms in expansion flows of shock-heated Ar and 1% N_2 + Ar mixtures are
described.   The measurements were made in a conical nozzle attached to the
end of a conventional shock tube.   For expansion flows of pure Ar from reservoir
temperatures of 3200° to 4200°K and a reservoir pressure of about 37 atm,
the measured Na temperatures ($\approx 2200°$K) were considerably in excess of the
local-translational temperature ($\approx 400°$K).   These high excitation temperatures
are interpreted in terms of the excitation of Na by free electrons produced
from ionization of the Na in the reservoir.   On this basis, free-electron tempera-
tures are deduced which indicate freezing of the electron thermal energy at
values corresponding to those expected at the nozzle throat.   This result
suggests a slow rate of transfer of electron thermal energy to the Ar transla-
tional mode.

        The addition of 1% N_2 to the Ar expansions produced large reductions
in the measured Na temperatures.   The reduced temperatures are shown to
correspond to the frozen N_2 vibrational temperatures expected on the basis
of previous results.   These reductions are explained in terms of an efficient
transfer of the excess-electron thermal energy to the N_2 vibrational mode,
the free-electron and N_2 vibrational temperatures being thereby coupled
and equilibrated during the expansion.

        The present results also substantiate the faster vibrational relaxation rates
inferred previously from similar expansion-flow studies of pure N_2; they
further suggest that the simple Landau-Teller rate equation, when used with
relaxation times measured in shock-wave flows, is not adequate to describe
the vibrational relaxation process under the extreme nonequilibrium conditions
associated with nozzle-expansion flows.

A. 7   On the Thermal Energy Transfer Between Free Electrons and Molecular
       Vibration, I. R. Hurle, J. Chem. Phys. <u>41</u>, 3592 (1964).

A. 7 cont'd.   Abstract

Thermally averaged probabilities for the electron de-excitation of the first vibrational level in N_2 are calculated from the discrete velocity-dependent collision cross sections measured by other workers. The results are presented for the electron temperature range 1000° to 5000°K. Over this range the probability is found to have an empirical temperature dependence of the form $AT^{-1.8} \exp(T^{1/3})$, with $A = 1.58 \times 10^{-3}$. The probability increases from 10^{-4} at 1000°K to 10^{-2} at 5000°K. By comparison, the corresponding experimental probabilities for the de-excitation of N_2 vibration by nitrogen molecules are 10^{-8} at 1000°K and 3×10^{-4} at 5000°K. These figures imply that in some circumstances an electron concentration of only 1 in 6×10^3 could do so at 5000°K. Existing spectrum-line reversal measurements of N_2 vibrational relaxation carried out in nozzle-expansion flows in the presence of small amounts of easily ionized Na and Cr atoms are reviewed in the light of these findings. It is shown that the electron concentrations in these experiments were too low to have significantly influenced the relaxation measurements.

The relative rates of degradation of electron kinetic energy to the translational, rotational, and vibrational modes of N_2 are considered on the basis of the above calculations. From these considerations it is proposed that in many nonequilibrium molecular systems the kinetic electron temperature will be closely coupled to the vibrational temperature of the molecules. Some results of current expansion-flow experiments which support this proposed coupling process are briefly mentioned, and its possible importance in relation to the extent of chemical and ionization nonequilibrium in other expansion flows of shock-heated air in hypersonic nozzles and around re-entry vehicles is discussed. It is suggested that free electrons, although present perhaps in small quantities, could be important in energy-degradation processes in these systems. Other existing observations in N_2 plasmas which appear to support the proposed coupling mechanism are reviewed.

A. 8   Importance of Impurities on Vibrational Relaxation Measurements in

   N_2, A. L. Russo, J. Chem. Phys. **44**, 1305 (1966).

A. 9   Spectrophotometric Measurements of the Vibrational Relaxation of CO

   in Shock Wave and Nozzle Expansion-Flow Environments, A. L. Russo,

   CAL Report No. AD-1689-A-8, July 1967.

A. 9 cont'd.   Abstract

Infrared and Na line-reversal spectrophotometric methods have been employed for the investigation of the vibrational relaxation of pure CO and 5% CO + 95% Ar test gas mixtures behind normal shock waves and in quasi-steady expansion flows. The shock-wave studies were conducted over a range of equilibrium shocked-gas temperatures of about 1400° to 3200°K and pressures of a few atmospheres. Vibrational relaxation times obtained by these two techniques were found to agree quite well and are consistent with other available shock-wave data for both test gas mixtures. The expansion-flow results for 5% CO + 95% Ar were obtained in a shock-driven conical nozzle for a range of reservoir temperatures of about 3500° to 5000°K and reservoir pressures of about 45 atm. For these experiments, the Na line-reversal and CO infrared diagnostic techniques indicated vibrational temperatures much lower than those predicted by the Landau-Teller theory using the shock-wave measured rate data. In addition, the infrared measurements indicated somewhat lower vibrational temperatures than the Na line-reversal results. In terms of vibrational relaxation rates, the expansion-flow data indicate that the deexcitation process in the nozzle proceeds about two orders of magnitude faster than anticipated on the basis of the rates measured behind shock waves. These observations are consistent with previous results obtained for N_2. While a conclusive explanation of these results is not presently available, the results of recent theoretical studies are discussed which suggest that the detailed mechanism of the relaxation process may depend on the gasdynamic environment.

A. 10 Spectrophotometric Measurements of the Vibrational Relaxation of CO in Shock Wave and Nozzle Expansion-Flow Environments, A. L. Russo, J. Chem. Phys. 47, 5201 (1967). Abstract as in A. 9 above.

A. 11 Resonance Absorption Spectrophotometry of the Hydrogen Atom behind Shock Waves, A. L. Myerson, H. M. Thompson and P. J. Joseph, CAL Report No. AD 1689-A-3, May 1964.

                    Abstract

The rate of formation of atomic hydrogen behind an incident shock wave in hydrogen-argon mixtures has been followed directly by means of atomic absorption spectrophotometry. The absorption involved the strong, resonance transition of the hydrogen atom from its ground state to the first excited level. The development of a cool, low pressure source of Lyman alpha radiation was required so that the half-width of the source line could be considered thin when compared with that of the same line in absorption arising from the hydrogen atoms behind the shock front. Preliminary rates have been calculated and provide evidence for dissociation catalyzed by oxygen.

A. 12 Resonance Absorption Spectrophotometry of the Hydrogen Atom behind
Shock Waves, A. L. Myerson, H. M. Thompson and P. J. Joseph, J.
Chem. Phys. 42, 3331 (1965).

A. 13 Atom Formation Rates behind Shock Waves in Hydrogen and the Effect
of Added Oxygen, A. L. Myerson, W. S. Watt and P. J. Joseph, CAL
Report No. AD 1689-A-7, November 1966.

Abstract

A direct, isothermal measurement has been made of the rate of formation
of atomic hydrogen behind shock waves in hydrogen-argon mixtures. This
has been accomplished by using atomic resonance absorption spectrophotometry
in the vacuum ultraviolet. The observations were made in an ultrahigh-purity
shock tube. The sensitivity afforded by the technique and the simplicity of
the interpretation bespeak a high degree of accuracy for the measurement.
The value $k_d = 1.18 \times 10^{12}\ T^{1/2} \exp(-94,500/RT)$ cm^3 $mole^{-1}$ sec^{-1} was
obtained over the temperature range 2150°K to 3640°K. Because of the sensitivity,
it was also possible to determine quantitatively the catalytic effect of the addi-
tion of small amounts of oxygen. These observations have led to an unequivocal
measurement of the rate of the limiting step $H + O_2 \longrightarrow OH + O$ in the mechanism
of the H_2-O_2 reaction under the conditions of the experiment.

A. 14 Atom Formation Rates behind Shock Waves in Hydrogen and the Effect
of Added Oxygen, A. L. Myerson and W. S. Watt, J. Chem. Phys. 49,
425 (1968).

Abstract

A direct isothermal measurement has been made of the rate of formation
of atomic hydrogen behind shock waves in hydrogen-argon mixtures. This
has been accomplished b using atomic resonance absorption spectrophotometry
at the Lyman-α line of both ^1H and ^2H . The observations were made in an
ultrahigh-purity shock tube. Absorption coefficients for the atoms were deter-
mined experimentally. The hydrogen-argon dissociation rate is given by the expression
$k_{H_2-Ar} = 2.23 \times 10^{12}\ T^{1/2} \exp(-92600/RT) cm^3$ $mole^{-1}$ sec^{-1} over the
temperature range 2290° - 3790°K. The hydrogen molecule was found to be
five times more effective than argon as a collision partner. Because of the
sensitivity of the technique, it was also possible to determine quantitatively
the catalytic effect of the addition of small amounts of oxygen. From these
observations an expression $k_{H-O_2} = 6.0 \times 10^{12}\ T^{1/2} \exp(-17750/RT)$ cm^3 $mole^{-1}$
sec^{-1} was obtained for the reaction $H + O_2 = OH + O$ over the temperature range
1700° - 2700°K.

A. 15 Atom Formation Rates behind Shock Waves in Oxygen, W. S. Watt and

A. L. Myerson, CAL Report No. AD-1689-A-9, February 1969.

Abstract

Atomic absorption spectrophotometry has been used to monitor the rate of oxygen atom formation behind shock waves in oxygen-argon mixtures. These observations were made by observing the time-history of absorption at the oxygen atom triplet near 1300 A. The atomic absorption coefficients were determined experimentally in the shock tube. These observations lead to an oxygen-argon dissociation rate given by $k_{O_2-Ar} = 1.85 (\pm 14\%) \times 10^{11} T^{0.5} \exp (-95,700/RT)$ cm^3 mole^{-1} sec^{-1} over the temperature range 2850°K to 5550°K. In addition this technique is shown to provide a powerful method for examining the vibration-dissociation coupling region. Measurements of the induction time for a steady-state atom formation rate to be established were obtained in the temperature range 2850°K to 5000°K. These measurements are compared with previously published experimental and theoretical induction times for dissociation in oxygen-argon mixtures.

A. 16 Atom Formation Rates behind Shock Waves in Oxygen, W. S. Watt

and A. L. Myerson, J. Chem. Phys. (to be published). Abstract as

in A. 15 above.

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